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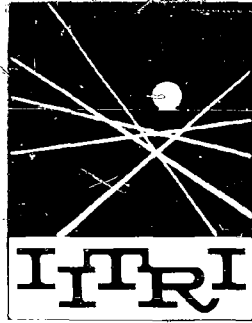
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Contract No. DA 11-ORD 022 3108

EMBRITTLEMENT OF METALS
BY ORGANIC LIQUIDS

ITRI-B183B2-4
(Summary Report)

Commanding Officer
Frankford Arsenal
Philadelphia 37, Pennsylvania

MIT RESEARCH INSTITUTE
Technology Center
Chicago 16, Illinois

Contract No. DA-11-ORD-022-3108

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MITR-183B2-4
(Summary Report)

December 1, 1962 - November 30, 1963

for

Commanding Officer
Frankford Arsenal
Philadelphia 37, Pennsylvania
Attention: Mr. J. M. McCaughey
Pitman Dunn Laboratories

January 2, 1964

MIT RESEARCH INSTITUTE

EMBRITTLEMENT OF METALS
BY ORGANIC LIQUIDS

ABSTRACT

High-strength steel and aluminum are shown to be embrittled in notched fatigue testing in the presence of water, alcohols, glycols, ethers, and aldehydes. It is shown that longer carbon chains, branching molecular shapes, and closed rings reduce the degree of embrittlement while multiplicity of $(-OH)$ or $(-O-)$ groups enhance it. By a variety of experiments and deductions, water is shown to behave more like a zero chain length organic molecule rather than an electrolytic medium.

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EMBRITTLMENT OF METALS BY ORGANIC LIQUIDS

I. INTRODUCTION

This is a summary report on progress of one portion of a composite program entitled "Fracture of Metals," identified under Contract No. DA-11 ORD 022 3108. This report covers the period December 1, 1962, to November 30, 1963.

This portion of the program on "Fracture of Metals" is directed toward exploring the existence and nature of embrittlement which might be produced by concurrent exposure of metals to organic liquids and tensile stresses. Organic liquids are defined for present purposes as pure liquid species, miscible liquids, and solutions of solids in liquids. Embrittlement constitutes the premature incidence of cracking as experienced under continuously increasing load, static loading, or dynamic (cyclic) loading. "Premature" is used here in the sense of a lower maximum load, a shorter time, or fewer cycles than would be expected for the material in air.

This research task has taken the position that the existing published knowledge on the subject is so sparse and questionable that the phenomenon has essentially to be rediscovered. The potential area of exploration involves combinations and permutations of diverse organic liquids, engineering metals, and systems of mechanical testing. Obviously there must be a simplification of approach. By analogy with experience in liquid-metal and stress-corrosion cracking, some very specific simplifications can be chosen. Two engineering metals have been chosen: Al and Fe—both offer the greatest potential spectrum of strengths and structures. One representative alloy of each metal was chosen which would be capable either by aging or by quench and temper, of producing high strengths by dispersion of fine particles in the structure. In the case of Al, the alloy 2024 has been chosen, heat treated to the T4 condition where it possesses a yield strength of 47,000 psi. The Fe counterpart was an air hardenable, high strength steel (commercial designation 300M^{*}).

^{*} 0.40% C, 1.6% Si, 0.75% Mn, 0.85% Cr, 1.85% Ni, 0.40% Mo, 0.08% V.

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quenched and tempered to a yield strength of about 200,000 ps. All previous experience points to these conditions as most likely to exhibit embrittlement.

Mechanical test systems, in increasing order of complexity, included:

- simple tensile test to failure
- failure under static loading at the yield point.
- cyclic loading of a sharply notched specimen.

By narrowing the material and test parameters, it was possible to conduct a wide range of explorations of the embrittling capabilities of organic liquids. The report which follows summarizes results and discusses their significance. Test procedures are summarized in detail in the appendix.

II. AN APPRAISAL OF LITERATURE

In recent years several summaries and interpretations of published works have appeared.⁽¹⁻⁴⁾ Each has reviewed essentially the same publications, but the interpretations of their significance differ somewhat. In recapitulation, the following is a list of phenomena revealed by various experiments which are pertinent to the topic under discussion.

(a) Reduction in the yield point of Sn, Al, and Pb single crystals immersed in surface active agents such as oleic acid, palmitic acid, and cetyl alcohol as dilute solutions in an inert solvent. These are the work of Rebinder and his associates. The work of Kramer does not confirm the effect on critical resolved shear stress in single crystals of Al but does confirm other effects such as work hardening and creep.

(b) Increase in the rate of creep of single crystals of Sn, Al, Pb, Zn, and Cd. The separate works of Rebinder, Masing, and Kramer are in essential agreement. There are long standing arguments in the literature based on work by Andrade and by Harper and Cottrell on the presence and significance of oxide films since all of this work has been done on very thin wire shaped specimens.

(c) The creep of polycrystalline wires is unaffected by the presence of organic species of surface active agents when the grain diameter of the metal is less than about 2% of the wire cross section, i.e., about 50 grains in a section.

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(d) A loss of 20-25% in the fracture strength of single crystals of Pb tested in solutions of active fatty acids and alcohols in a neutral solvent at very high strain rates only.

(e) Discontinuous changes in creep rate and flow stress of both single crystal and polycrystalline aluminum subjected intermittently to electrolytic dissolution. The effect is proportional to the electrolytic current or rate of dissolution.

(f) Influence of imposed electrolytic potential on the hardness of Tl, Te, and Cd, which include increases and decreases of hardness. The presence of surface adsorbing alcohols accentuates the effect of potential. The phenomenon is called the Electro Capillary Effect by Rebinder.

(g) Reduction of the order of 25-50% in fatigue strength and endurance limit of ferritic steels immersed in vaseline oil solutions containing isoamyl alcohol or oleic acid. Simple high-purity water can produce the same deterioration by what is termed "corrosion-fatigue". The addition of isoamyl alcohol to water reduces the rate of corrosion yet perpetuates the fatigue strength loss and provides a distinguishable and separable effect.

There are various proposed mechanisms for these effects. The Rebinder group prefer the concept that physical adsorption of polar molecules of certain species lowers the surface energy of the solid leading to two effects: reduction of the magnitude of barriers to slip at the surface leading to accelerated yielding, and reduction of the cleavage energy at the surface leading to cracking. Simple chemical dissolution or electrolytic polishing can, in principle, raise or lower the flow stress, depending on the nature of the surface material. If the surface constitutes an oxide film, and/or structurally irregular material, the surface dissolution will naturally lead to a reduced flow stress but generally only in fine wire or foil where the crystal size is not much smaller than the thickness or diameter dimension. In brittle materials where cleaved surfaces have a high population of slip sources, the removal of these by chemical dissolution can clearly lead to magnified strength.

Recent experiments by Kramer,⁵⁾ on Al alloy specimens of large dimensions compared to their grain size, suggest that simple material removal models are inadequate, for it was shown that certain reversible yield

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stress drops occurred with the imposition of electrolytic current. The effects were very small, simply because a change in the flow stress of the surface material can have only a small effect on the average flow stress of the specimen. These results seem to be related to the Rebinder electro capillary effect.

There is an intermediate effect involving chemical attack of the metal by the liquid environment which produces a metallo-organic species, which in turn has the character of a surface active agent. Kramer's studies on metal stearates and stearic acid and other organic acids justify a process of change of mechanical properties by chemisorption.

The influence of environment on the plastic flow properties of metals has questionable relevance to present interests in the fracture of normally ductile metals. The most interesting experiments in this field are those by Karpenko on the dynamic fatigue strength of steel in surface active liquid environments. It is useful at this point to recapitulate his results

steels:	0.15-0.25% C, 0.7-1.0% Cr 0.35-0.45% C, 0.5-0.8% Mn, 0.8-1.1% Cr.
condition:	quenched and tempered, undesignated strength annealed, UTS = 70,000 psi
media:	air, water, water + 2% isoamyl alcohol, inactive vaseline oil + 2% isoamyl alcohol or 2% oleic acid, commercial lubricating oil, new and spent, lubricating oil + 2% oleic acid.

Compared to the endurance limit in air, the endurance limits in water, water + isoamyl alcohol, vaseline oil + isoamyl alcohol or oleic acid, and lubricating oil + oleic acid are measurably lower. Water is as effective as any of the surface active agents by generating what is known as corrosion-fatigue. The corrosion process can be stopped (at least by visual inspection) by the addition of small amounts of isoamyl alcohol as an inhibitor. The surface active character of isoamyl alcohol is sufficient to produce just as severe loss in endurance limit. There is a distinction between corrosion fatigue and surface active agent fatigue. In the former case there is no defined endurance limit, whereas in the latter a clearly resolvable limit is measured. This signifies that fracture in the presence of surfactants (a

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term commonly used for surface active agents) is dependent on the conjoint existence of a minimum stress and a minimum activity. In corrosion fatigue no critical stress limit exists.

The amount of isoamyl alcohol in water is not critical between 0.2 and 2% concentration. The loss in endurance limit in annealed steels is only about 10%. At an intermediate hardness level, the loss increases to about 20%, and at higher hardness levels (probably $UTS \approx 150,000$ psi) the loss in endurance limit is nearly 50%. Thus, the harder the steel, the more prone it is to embrittlement. This is in agreement with all other environmental embrittlement phenomena. Certain commercial oils have mild surfactant properties with consequent loss in endurance limit. There were no observed differences between new and spent oil. In the presence of a strong surfactant, specimen finish becomes an unimportant factor, whereas in normal testing, it is a definite factor.

The rate of cycling in fatigue testing is an important factor of life time in the presence of a surfactant. The lower the rate of cycling, the more effective is the embrittlement. For example, water + 2% isoamyl alcohol lowered the endurance limit by 7% at 10,000 cpm and by 30% at 3000 cpm. This is an important observation, for it indicates that the process is controlled by the rate at which the surfactant can move in cracks. Although the work of Karpenko is at least ten years old, it has never been repeated.

III. SERIES OF EXPERIMENTS

A. Tensile Testing in the Presence of Organic Liquids

All engineering metals (except certain of the precious species) are covered with continuous films of oxide. As a result of high temperature, these films may be so thick that the metal is black or otherwise nonmetallic in appearance. However, under proper conditions of surface preparation, the oxide film is so thin that the natural color and reflectivity of the metal is readily apparent. Though only a few hundred angstroms thick, these oxide films are effective barriers, separating the metal from gaseous or liquid environments. It is very difficult to conceive of a scheme whereby an organic liquid can be brought to an oxide-free surface. The ease and reproducibility

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of such a task are so dubious that an exploration program must find some alternative approach.

In simple tensile testing, the oxide film barrier is not really a major problem. Oxide films are not ductile, and on exceeding the yield point of the substrate metal, the film must crack repeatedly. Provided that the surface of the specimen is liberally swabbed with the candidate organic liquid, the cracks which form provide repeated lines of contact between the metal and the liquid. Tensile strain-strain studies were conducted over the whole range of elastic-plastic behavior.

More than 200 organic liquids and solutions were used in tensile test experiments with the Al and steel materials. Each of these species fell under one of the following categories:

- Hydrocarbons
- Alcohols
- Ethers
- Aldehydes
- Ketones
- Esters
- Organic acids
- Metal salts of organic acids
- Ketoxamines
- Amines
- Halogenated organic compounds
- Metal-organic compounds
- Commercial organic surfactants

In substance, no influence of any organic liquid was found on the tensile behavior of high-strength Al and steel. Tensile behavior includes yield point, rate of work hardening, ultimate tensile strength, total elongation, and final reduction in area.

B. Failure of Unnotched Specimens under Static Loading

Embrittlement which depends on chemical adsorption, and/or reaction at the crack root, and on rate of transport of the active fluid

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down the crack to the root may not be revealed by a tensile test. It is necessary to apply a time axis to the process. In such circumstances, a static loading arrangement is an accepted practice.

The problem of the oxide film barrier is not so simply dealt with here. There is some possibility that oxide films themselves crack progressively over a period of time when the metal substrate is loaded in tension to the yield point, but there is no actual knowledge of this. Alternatively, one can introduce into the liquid medium a corrosive agent which will progressively deteriorate the continuity of the oxide film. A further method is to scrape or cut the surface of the specimen with a sharp tool under a thick film or actual pool of the candidate embrittling liquid.

All of these methods were tried on simple bend specimens loaded to the yield point at the tensile surface. Exposure time of 7 days was allowed for failure to occur. A 5% saline solution was used as the corrosive medium and as a solvent for organic species where possible.

The embrittlement propensity of more than 200 organic species and a large number of saline solutions under the specific test circumstances were explored. There was no single instance of failure under static loading. This was true even for those conditions where considerable corrosive action was apparent. This phase of the program embraced both high strength aluminum and steel.

C. Influence of Water on Dynamic (Cyclic) Fatigue

Cyclic fatigue of deeply edge-notched sheet specimens under tension-tension stressing in the presence of candidate embrittling agents produced systematic and pronounced trends of premature failure. In this case, premature failure is judged in terms of the number of cycles to failure in the presence of the active liquid as compared with testing in air under identical stressing conditions.

Fatigue stressing has the special attribute of combining applied stress, slip (plastic strain), and cracking activity over a substantial period of time. Thus, chemical interactions and surface wetting processes involving the candidate surfactant liquids have considerable time to occur and to exert influence.

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Fatigue failure can be described by plotting the number of cycles to failure against the cyclic component of stress. This plot is commonly known as the S-N curve. Steel has the special attribute of an endurance limit—an alternating stress magnitude below which failure will never occur. Edge-notched sheet specimens with a filed 0.001 in. root radius have been tested in tens on tens on fatigue. That is, a constant tensile stress is maintained on the specimen with a superimposed addition which cycles between zero and some maximum value. The S-N curve plotted in Figure 1 for the high strength steel relates the magnitude of the cyclic maximum to the number of cycles to failure. There is a sharp and clearly defined endurance limit. The cracks originate from one or both of the edge notch roots and propagate in a direction transverse to the axis of stressing until the maximum stress exceeds the ultimate strength of the remaining cross-section. About 50% of the total crack surface represents slowly advancing fatigue crack.

The action of a liquid environment is induced by clamping two liquid saturated asbestos pads to the faces of the specimen over the whole notched area. A "Saran Wrap" or polyethylene envelope prevents volatilization. The solid points in Figure 1 demonstrate the ability of a 5% NaCl solution to depress the endurance limit and perhaps even to eliminate it. This is a simple confirmation of previous Russian work.

As a basis for screening the effectiveness of a large number of organic liquid candidates, a single stress level has been chosen. This stress level is near, but below, the normal endurance limit. Thus, a specimen dry and in air will not fail at this stress level even after many millions of cycles. However, at this stress level, a 5% NaCl water solution will cause failure in 300,000-600,000 cycles. The effectiveness of other liquids can be judged by reference to these two comparative conditions.

The S-N curve for the high strength Al alloy, shown in Figure 2 does not possess a true endurance limit. Therefore, the ratio of fatigue life in salt solution to that in air is finite at all stress levels and not appreciably variable. A dynamic stress increment of 1210 psi to a 8050 psi preload was chosen at which the Al alloy specimen fails in air at about 4,000,000 cycles and in salt solution at about 2,500,000 cycles.

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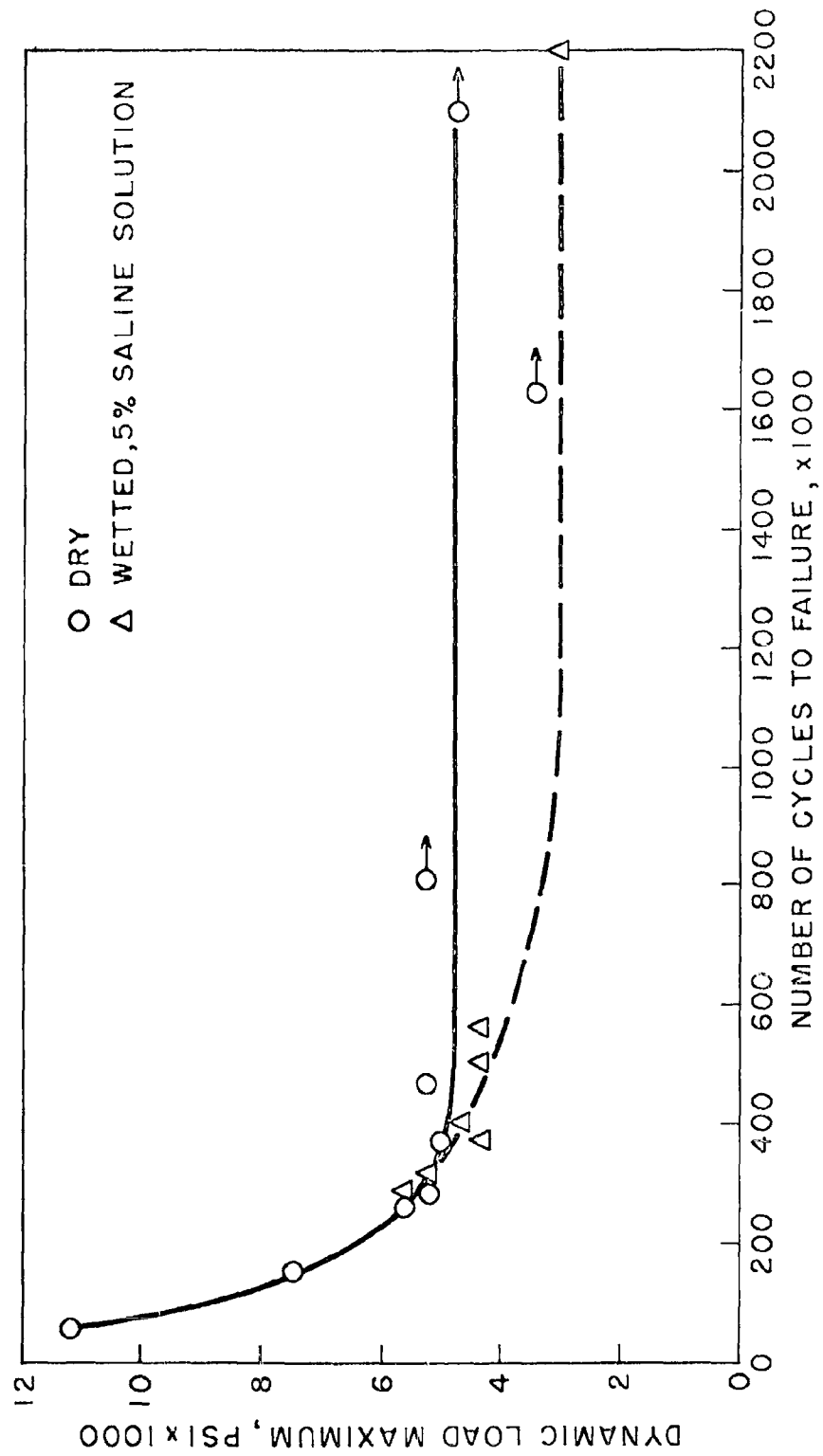


FIG. 1 - FATIGUE FAILURE (S-N) CURVE FOR HEAT-TREATED STEEL (200,000 PSI YIELD STRENGTH) UNDER A STATIC NOMINAL STRESS OF 12,500 PSI AND A VARIABLE DYNAMIC NOMINAL STRESS AT 1800 CPM.

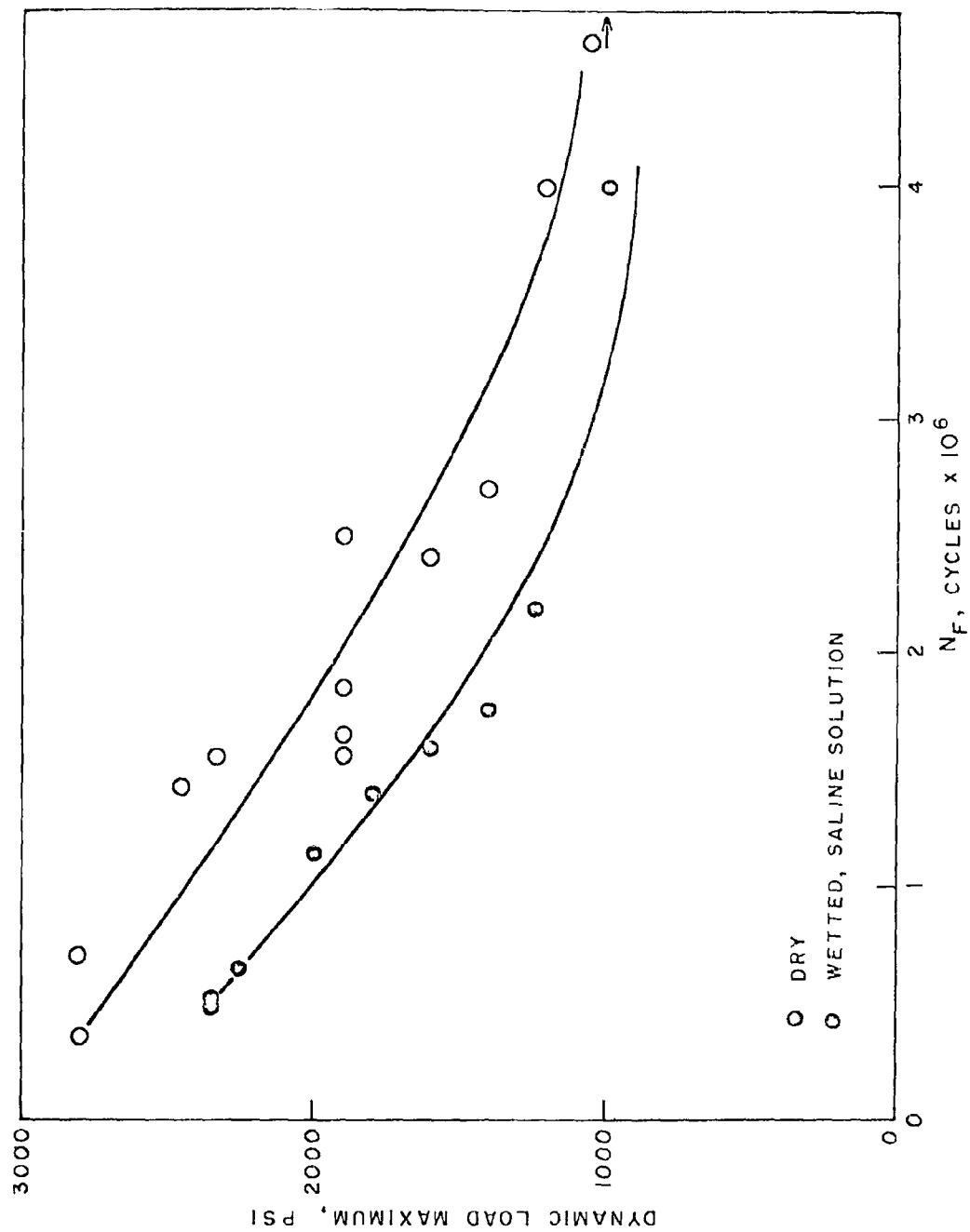


FIG. 2 - FATIGUE FAILURE OF AL 2024-T4 UNDER A STATIC NOMINAL STRESS OF 3050 PSI AND A VARIABLE DYNAMIC NOMINAL STRESS AT 1800 CPM.

Distilled water induces fatigue failure in the high strength steel under the specific conditions of test at 583,000 cycles. This is a profound embrittlement but one which is no novelty to the subject of high strength steels. The origin of water embrittlement has been generally regarded as falling within the context of what is termed "stress corrosion" cracking. Contemporary theory of stress-corrosion cracking treats the mechanism as one of highly localized electrochemical corrosion, accelerated and guided by the intensity and direction of principal tensile stresses.

However, the substance of the present results sheds considerable doubt on the applicability of stress-corrosion theory to water embrittlement. The addition of 5% NaCl to water as a solution produces fatigue failure in 530,000 cycles, which is not distinguishable from the results with distilled water. Yet, clearly, the electrical conductivity of the saline solution is greater than that of distilled water.

Further tests reveal no significant influence of pH of water on fatigue limit. Distilled water exposed to air assumes a pH of about 4, probably because of CO_2 adsorption in minute amounts. The pH of distilled water was adjusted to a value of 1 by the addition of a few drops of HCl in one instance and to a value of 7 and 12 by the addition of drops of concentrated NaOH solution. The results of fatigue testing using these four pH levels are shown in Figure 3, where over the range of pH from 1 to 12, the influence of hydrogen and hydroxyl ion concentration is very small and probably negligible when the normal scatter of fatigue data is taken into consideration. Added to the negligible influence of a high salt concentration, ion concentration is not a significant factor. This conclusion is, of course, quite incompatible with contemporary stress corrosion theory.

To these results may be added the behavior of large imposed potentials between the specimen and a platinum wire through the medium of distilled water while undergoing cyclic fatigue stressing. These potentials are high enough to promote rapid drift of ions to one or another electrode depending on the sign. If ion mobility is a significant factor, there should be a significant shortening of fatigue life. The results are as follows:

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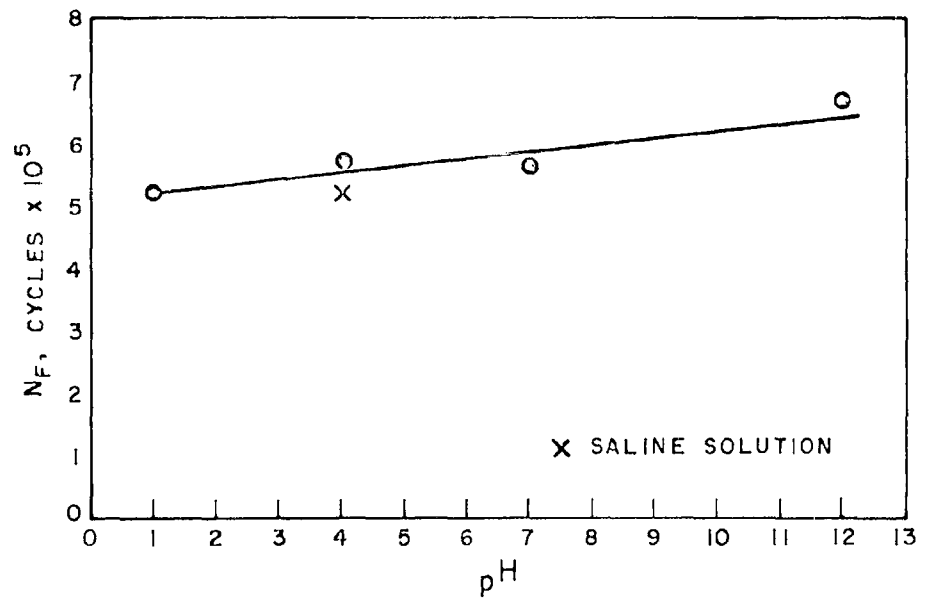


FIG. 3 - INFLUENCE OF THE pH OF WATER ON THE FATIGUE LIMIT OF HIGH-STRENGTH STEEL V-NOTCHED TENSION-TENSION SPECIMEN. (12,500 psi preload, 4370 psi dynamic load.)

Potential	N_F , cycles to failure
zero	535,000; 601,000
specimen negative, 2 volts DC	421,000; 470,000
specimen positive, 2 volts DC	516,000; 585,000; 912,000

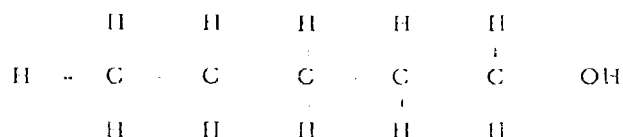
With the test specimen positive to attract (OH^-) ions, there is no significant influence by a large potential. When connected negative to attract (H^+) ions, there is an approximately 20% decrease in fatigue life which is a relatively small effect and most likely due to hydrogen absorption into the steel rather than to corrosive action associated with the plating of hydrogen. Again we must conclude that ions and ion concentration do not play a dominant role in fatigue failure.

A similar conclusion can be drawn from the relative embrittling action of distilled water and 5% saline solution on high-strength aluminum. In distilled water, the 2024 alloy fails in about 2,650,000 cycles whereas with the saline solution failures occurred in the range of 2,200,000 to 2,500,000 cycles. The difference is trivial despite the fact that the saline solution is clearly highly corrosive and the distilled water is not.

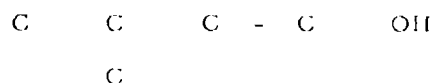
D. Influence of Alcohols on Cyclic Fatigue

The saturated alcohols are non-ionic and can be described by the general formula $C_nH_{2n+1}OH$, so that when $n = 1$ we have CH_3OH (which is methanol) and when $n = 8$ we have $C_8H_{17}OH$ (which is octyl alcohol). However, the formula $C_8H_{17}OH$ satisfies a whole group of alcohols of similar molecular weight but different physical properties. The different physical properties derive from variations in symmetry of carbon and hydroxyl bonding.

The primary, secondary, and tertiary alcohols each have a common property defined in terms of the coordination of carbon atoms around the carbon atom to which the $(-OH)$ group is attached. The carbon atom associated with the $(-OH)$ group in primary alcohols has a carbon coordination of one; in secondary alcohols, a carbon coordination of two; and in tertiary alcohols a carbon coordination of three. Thus, one of the primary amyl alcohols could be described as follows:

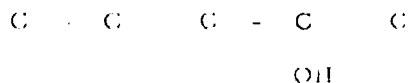


but a simple variation such as

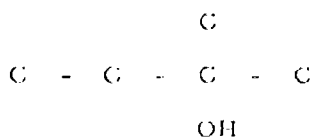


(for simplicity, the hydrogen atoms are omitted) does not change the carbon coordination at the (-OH) group and so constitutes another primary amyl alcohol with different physical properties. The first of these is commonly called n-amyl alcohol and for obvious reasons is described as a straight chain alcohol. The second is called isoamyl alcohol.

The straight chain secondary alcohol - sec-amyl, has the following arrangement (again omitting hydrogen atoms) between carbon atoms and the (-OH) group:



The carbon coordination of the carbon atom holding the (-OH) group is two. When this becomes three, as follows



we have tert-amyl alcohol which is, strictly speaking, no longer a straight chain molecule.

Obviously the multiplicity of alcohol species goes up with molecular weight, and a study of embrittlement might get mired in irrelevancies if every species was taken for study. For the purpose of this program, simplified trends are the objective.

A clear and simple trend is revealed by plotting the cycles to failure against the numerical value of n from the formula $C_nH_{2n+1}OH$ as in Figure 4. Two curves are plotted -- one for the primary and one for the secondary alcohols.

It is most remarkable that when the curves for both primary and secondary alcohols are extrapolated back to $n = 0$ the value of N_F coincides almost exactly with that for distilled water. For the purposes of embrittlement, this suggests that water behaves as a limiting species of alcohol. This is another strong indication that stress-corrosion concepts are inapplicable.

While the correlation of fatigue life with the number of carbon atoms in the alcohol molecule is a valuable sign of systematic behavior, it does not of itself shed much light on the mechanism of embrittlement. The common denominator in all of these alcohols is the existence of an $(-OH)$ group. But the oxygen atom is about four times as big as the hydrogen atom so that the $(-OH)$ group is really dominated by the size of the oxygen atom and might be regarded effectively as such. Since metals have a strong affinity for oxygen, it is reasonable to suggest that active influence of alcohols on the cohesive strength of iron derives from interaction between surface atoms of iron and the $(-OH)$ groups of alcohol. The influence of the $(-OH)$ group can be seen from a comparison of ethanol (C_2H_5OH), whose number of cycles to fracture (N_F) was 935,000, with ethylene glycol, $(HO-C_2H_4-OH)$, whose structure is very similar but possesses two $(-OH)$ groups. In this case the number of cycles to failure (N_F) is 824,000.

While the secondary alcohols are consistently more active than the primary alcohols, the tertiary alcohol reverses this trend abruptly.

Alcohol	N_F , Cycles
n-amyl	1,075,000
iso-amyl	1,172,000
sec-amyl	892,000
tert-amyl	1,530,000

As will be discussed later, this probably reflects the sharp drop in packing efficiency in going from molecules with one- or two-dimensional characters to those with three-dimensional characters. A further insight into the influence of molecule size and shape may be had by examining the behavior of

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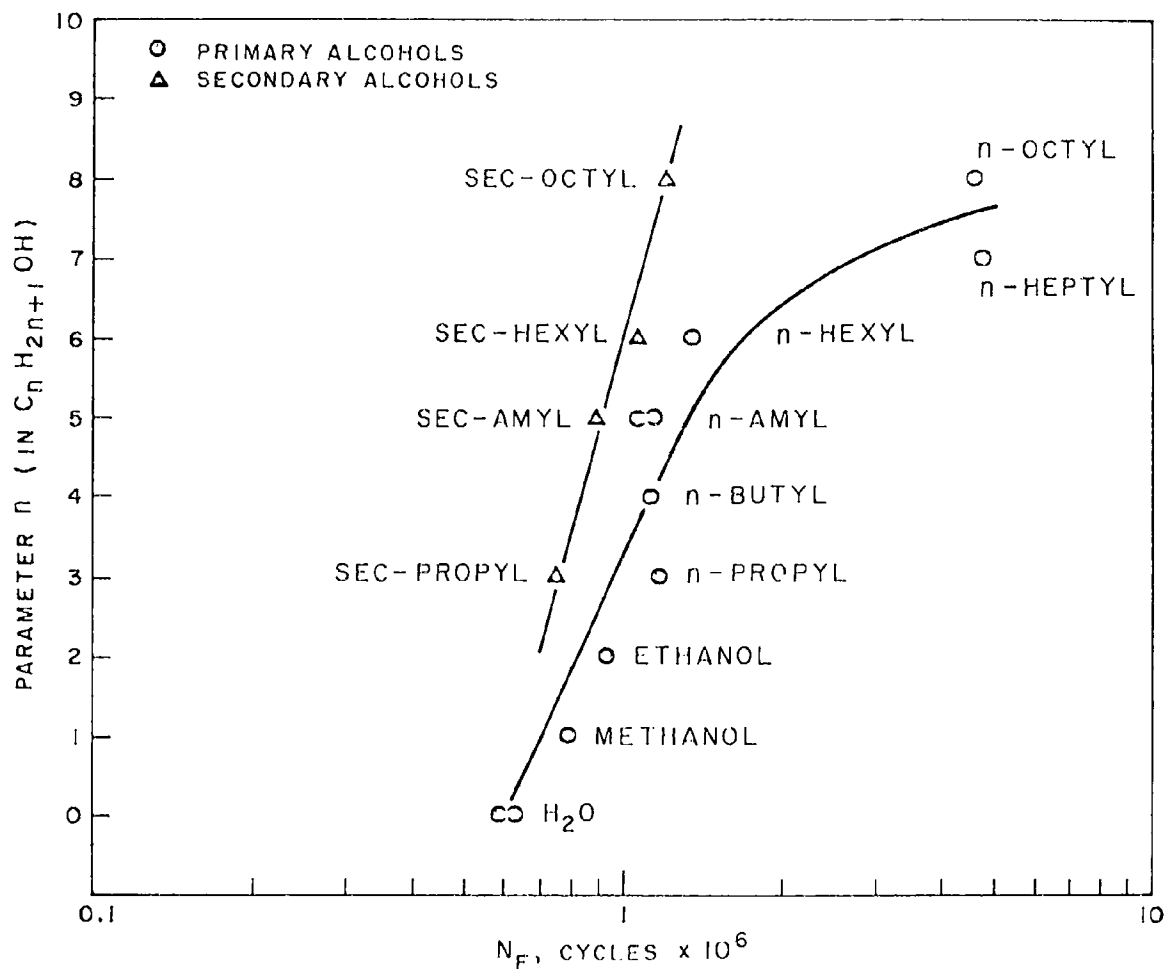


FIG. 4 - FATIGUE LIMIT (N_F) OF HIGH-STRENGTH STEEL IN PRIMARY AND SECONDARY ALCOHOLS. (V-notched tension-tension specimens, 12,500 psi preload, 4370 psi dynamic load.)

benzyl alcohol. Benzyl alcohol can be regarded as methanol with an attached benzene ring. This has a definite effect in reducing embrittlement, for while methanol causes failure in 796,000 cycles, benzyl alcohol requires 1,133,000 cycles.

The alcohols provide a similar trend when applied to high-strength aluminum. The results of a program of testing primary and secondary alcohols are shown in Figure 5. Again, as longer chain molecules are used, the embrittlement factor progressively disappears. The octyl alcohols are essentially nonembrittling. There is no resolvable distinction between primary and secondary alcohols. Finally, as with steel, extrapolation to zero carbon chain length coincides with the fatigue life of the alloy in water. Again, we have evidence that water behaves as a limiting alcohol species.

In going from a pure liquid species to liquid solution, we open up at least two interesting alternatives:

- solution of an active component in an inactive solvent
- miscible solution of two components of different activity.

Examples of each are shown in Figures 6 and 7.

Figure 6 illustrates the behavior of solutions of an active component, isoamyl alcohol, with an inactive component, heavy mineral oil. The trend shows an independence of concentration of the isoamyl alcohol above a critical 10% level. This is the expected behavior of a solution in which one component has a propensity for surface adsorption. The existence of a threshold concentration requires some consideration. In vapor condensation processes, the desorption and absorption rates usually have different concentration dependences, and as a result, the equilibrium concentration of isoamyl molecules on the iron surface achieves a saturation level only at some finite solution concentration.

Figure 7 illustrates the behavior of two miscible active liquids, water and ethanol. The shape of the curve indicates that water adsorbs to an iron surface to a degree in excess of its proportion in the solution. It may be that all solutions of active components will show this characteristic. If this is the case, then it can be inferred that the adsorption bond strength and embrittling propensity are directly proportional.

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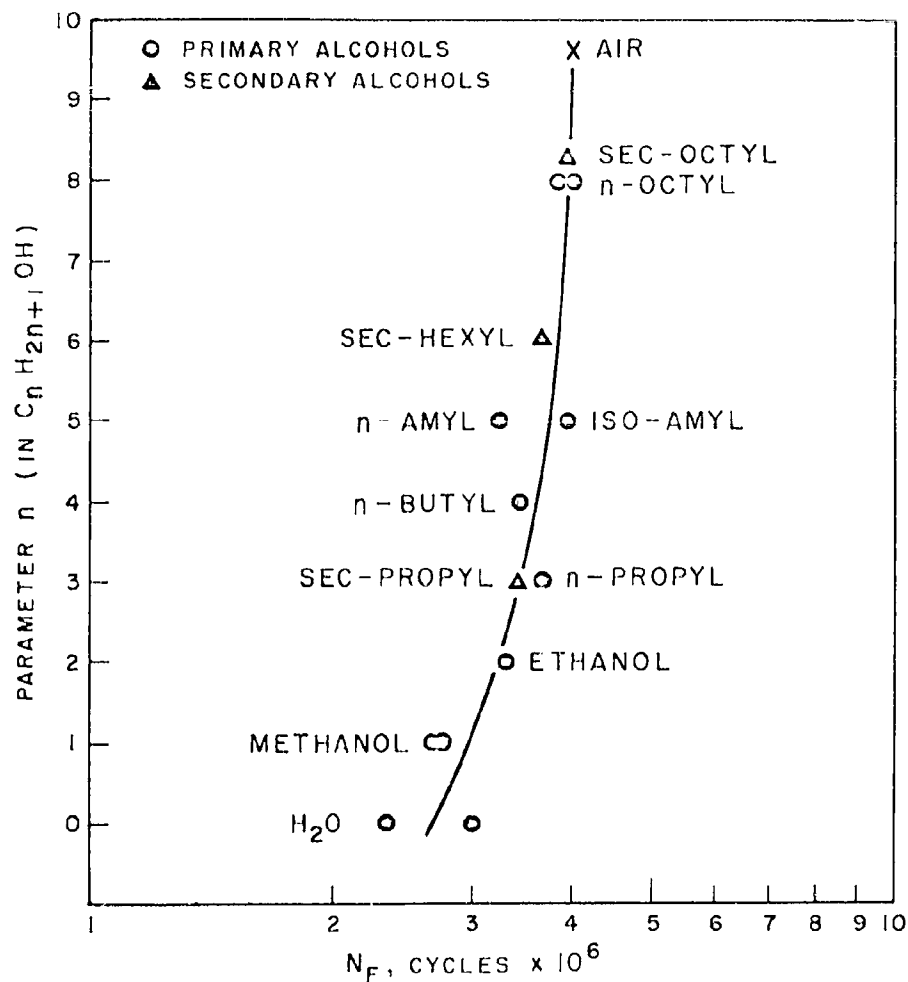


FIG. 5 - FATIGUE LIMIT (N_F) OF HIGH-STRENGTH ALUMINUM IN PRIMARY AND SECONDARY ALCOHOLS. (V-notched tension-tension specimens, 8050 psi preload, 1210 psi dynamic load.)

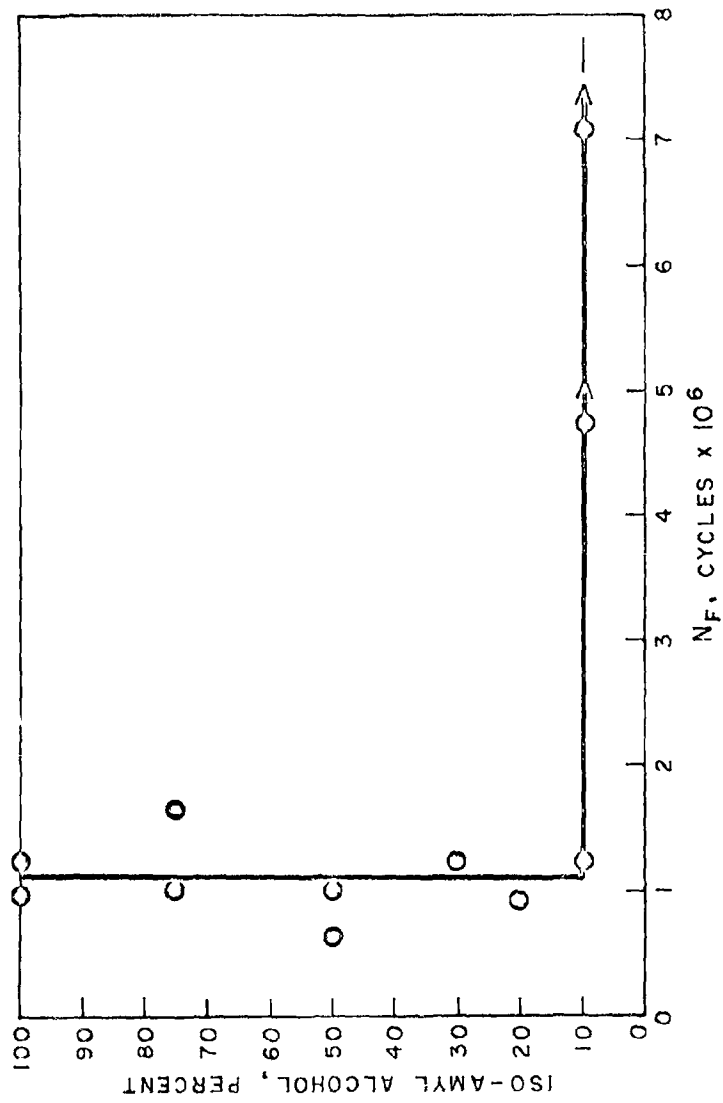


FIG. 6 - FATIGUE LIMIT (N_F) AS A FUNCTION OF ISO-AMYL ALCOHOL CONCENTRATION IN HEAVY MINERAL OIL. (High-strength steel, V-notched tension-tension specimen, 12,500 psi preload, 4370 psi dynamic load.)

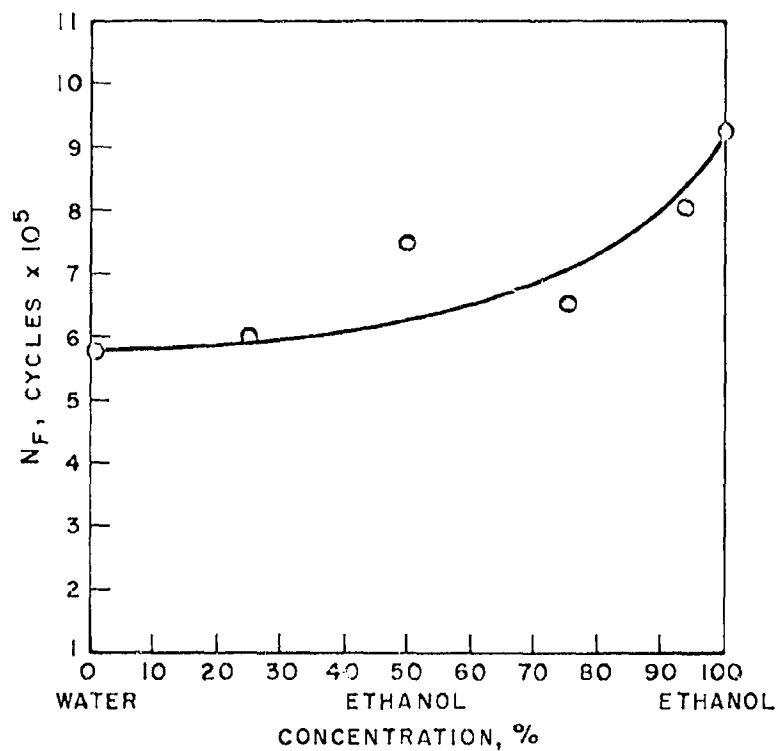
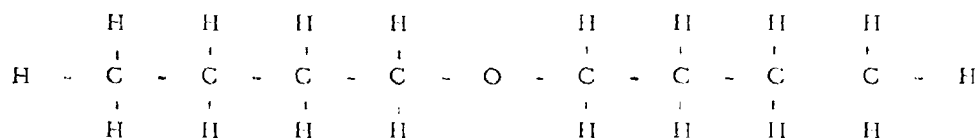


FIG. 7 - FATIGUE LIMIT (N_F) IN WATER-ETHANOL SOLUTIONS. (High-strength steel, V-notched tension-tension fatigue specimen, 12,500 psi preload, 4370 psi dynamic load.)

E. Influence of Ethers on Cyclic Fatigue

The simple di-ethers can be described by the general formula $C_n H_{2n+1} O C_n H_{2n+1}$ so that when $n = 1$ we have CH_3OCH_3 which is n-methyl ether and when $n = 8$ we have $C_8H_{17} O C_8H_{17}$ which is n-octyl ether. There are many ether variations based on the choice of hydrocarbon group on either side of the (-O-) group and on a multiplicity of (-O-) groups in a chain.

The molecular formula for a primary di-ether does not adequately describe it for present purposes. We can alternatively write n-butyl ether as:



The carbon atoms are completely shielded by hydrogen atoms but the oxygen atom is not symmetrically bonded on all sides. The ethers may thus be regarded as polar molecules possessing a polarizable oxygen atom, i.e., an oxygen atom whose force field has some measure of ability to interact with other incompletely shielded force fields such as exist at the surface of solids.

The primary di-ethers are capable of producing embrittlement in steel under cyclic fatigue. Figure 8 demonstrates that as with alcohols, the degree of embrittlement is proportional to the carbon chain length. There is a remarkable similarity between the primary di-ethers and the secondary alcohols in their respective absolute measures of embrittlement and the rate of change with carbon chain length. The general similarity between ethers and alcohols leads to the inference that the polar properties of the (-OH) and (-O-) groups are not very much different. Again, it is seen that extrapolation (Figure 8) to zero carbon chain length coincides with the measure of embrittlement exhibited by distilled water.

It appears that multiple polar oxygen groups (-O-) can compensate for long carbon chain length so that embrittlement activity is equivalent to simple ethers of short carbon chain length. Three examples (hydrogen atoms omitted) are:

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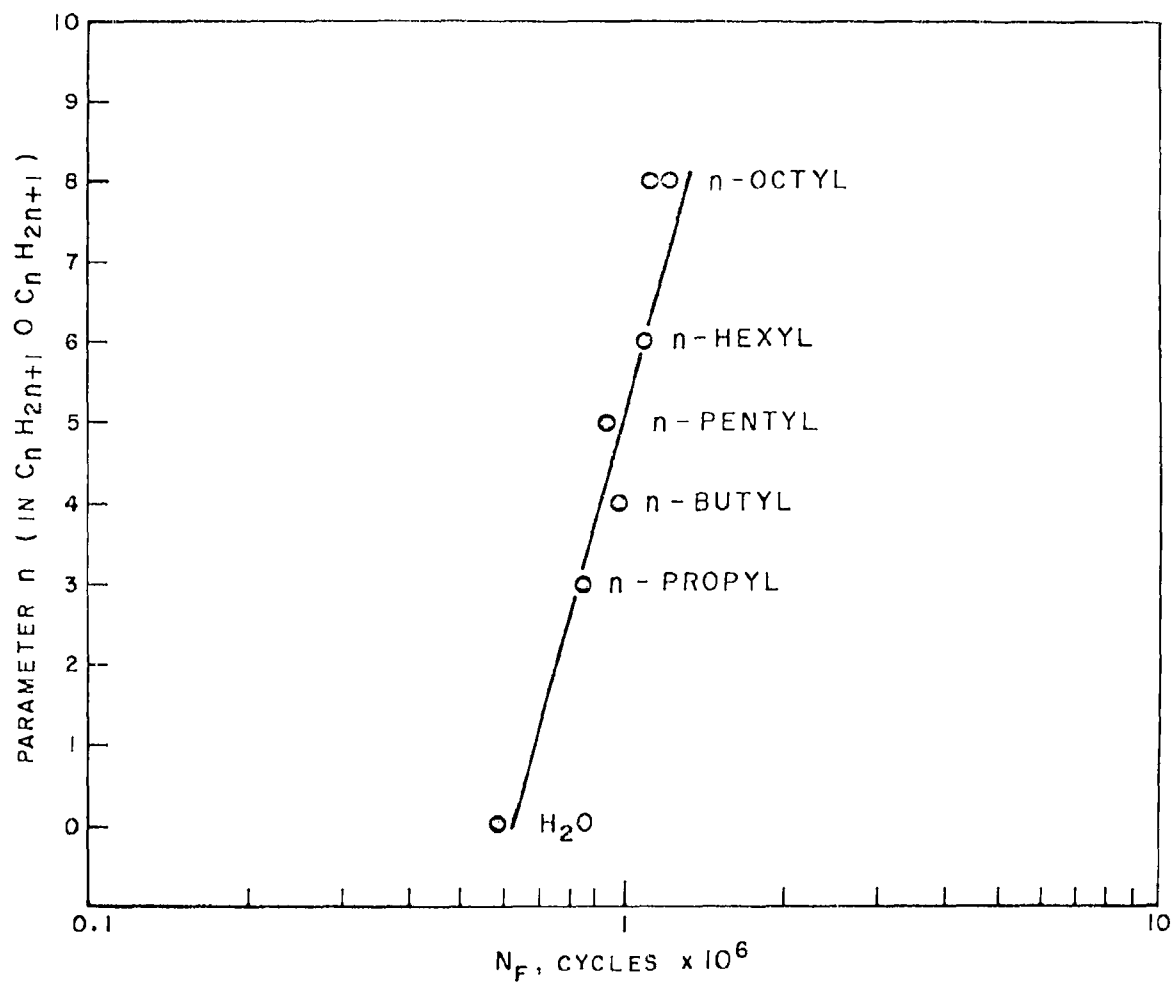


FIG. 8 - FATIGUE LIMIT (N_F) IN SIMPLE ETHERS. (High-Strength steel, V-notched tension-tension specimens, 12,500 psi preload, 4370 dynamic load.)

diethylene glycol diethyl ether $N_F = 706,000$ cycles.
 $C-C-O-C-C-O-C-C-O-C-C$

diethylene glycol dibutyl ether $N_F = 807,000$ cycles.
 $C-C-C-C-O-C-C-O-C-C-O-C-C-C-C$

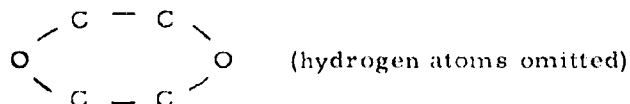
diethylene glycol mono-n-hexyl ether $N_F = 816,000$ cycles.
 $HO-C-C-O-C-C-O-C-C-C-C-C$

These failures are comparable to those produced by n-propyl and n-butyl ethers. Note that the (-OH) is acting as equivalent to an (-O-) group.

A similar indication of the significance of multiple polar groups is obtained by comparing the cycles to fracture produced by ethanol, n-propyl alcohol, ethylene glycol, diethylene glycol, and glycerol:

ethanol	$C-C-OH$	900,000 cycles
n-propyl alcohol	$C-C-C-OH$	1,040,000 cycles
ethylene glycol	$HO-C-C-OH$	824,000 cycles
diethylene glycol	$HO-C-C-O-C-C-OH$	756,000 cycles
glycerol	$\begin{array}{ccccc} C & - & C & - & C \\ & & & & \\ OH & & OH & & OH \end{array}$	868,000 cycles

On the other hand, a closed chain system has no effect. Dioxane is a case in point, with a bond arrangement as follows:



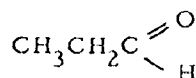
Here we have two polar (-O-) groups arranged in a closed chain. Dioxane produced no embrittlement in steel to the extent that failure had not occurred after 7,600,000 cycles.

A check on the possible interference of absorbed water as a trace impurity was made in the case of diethylene glycol dibutyl ether by the use of infrared spectral absorption analysis. Inspection of the absorption bands showed no detectable evidence of either alcoholic (-OH), water, or carbonyl groups ($C=O$) at 3 and 5.86 microns, respectively. Almost all other test materials were dried before use.

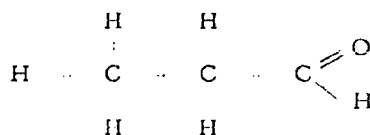
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F. Influence of Aldehydes on Cyclic Fatigue

The aldehydes are hydrocarbon chains to which is appended a group. Thus propanal is a propyl chain with the appropriate end group:



or



The oxygen atom has a double covalent bond with its adjacent carbon atom, and embrittlement studies provide an opportunity to assess the relative polarizability of an (=O) atom as compared to a twofold single covalent bond as in ethers.

<u>Ether</u>	<u>Aldehyde</u>	<u>N_F, cycles</u>
n-propyl		840,000
	propanal	1,050,000
n-pentyl		950,000
	pentanal	1,400,000
n-heptyl (interpolated)		1,200,000
	enanthal	1,500,000

There is a consistent trend to indicate that the (=O) group is somewhat, but not markedly, weaker than the (-O-) group in surface activity. As with the alcohols and the ethers, Figure 9 shows a consistent relationship between embrittlement and carbon chain length which extrapolates to the value for water at zero chain length.

G. Failure of Notched Specimens Under Static Loading

One can wonder whether the premature failures encountered by cyclic stressing in an environment of an active organic liquid is due more to the cycling action than to the peak stresses. It is likely that the continual elastic opening and closing of a notch and subsequent crack will rupture oxide

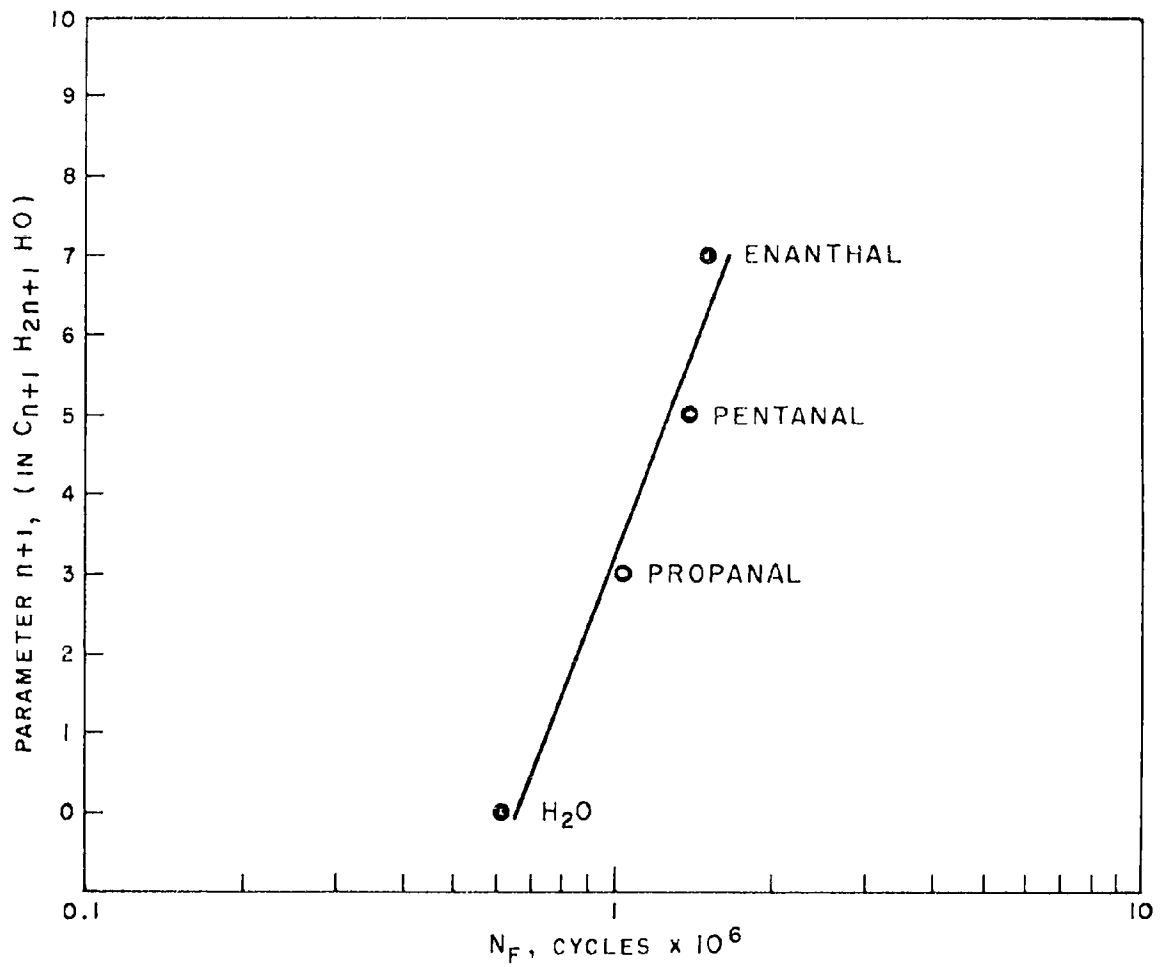


FIG. 9 - FATIGUE LIMIT (N_F) IN ALDEHYDES. (High-strength steel, V-notched tension-tension specimens, 12,500 psi preload, 4370 psi dynamic load.)

films as they form and perpetuate liquid metal contact. But this is only speculation. It was appropriate, therefore, to use the same center notched specimen with the same system of wetting with a liquid under conditions of static loading. In this case, a stress of 90% of the ultimate strength was used. In air the specimen sustained this load for many days without failure. Wetted with water, average failure times were about 8 hours. Wetted with methanol, the failure time averaged about 9 1/2 hours. No failures were encountered with ethanol or propanol despite exposures of as long as 48 hours.

We may conclude that while stress itself can cause failure, the process is very protracted. The cyclic stress action of dynamic fatigue is an important factor in embrittlement.

IV. SUMMARY OF EXPERIMENTAL OBSERVATIONS

1. Embrittlement by organic liquids is not encountered in simple continuous loading in tension to failure and in static loading of unnotched specimens at stresses as high as the yield point. Only water and methanol produced premature failure in static loading of edge-notched specimens loaded in tension. Cyclic loading in tension-tension fatigue of edge-notched specimens produced premature failures which were systematically related to the molecular structure of the organic liquid.

2. Water proved to be the most effective embrittling liquid in cyclic fatigue testing. Ion concentration by adjustment of pH, by addition of soluble NaCl, or by imposed DC potential has, at most, a minor influence on the effectiveness of water as an embrittling agent of steel. In the case of aluminum, the highly corrosive saline solution was only slightly more effective than distilled water.

3. The embrittling action of primary and secondary alcohols is proportional to the carbon chain length, being more effective at the shortest carbon chain length. Tertiary alcohols and closed chain alcohols (benzyl) are less effective than primary or secondary alcohols of equivalent carbon chain length. A glycol with an (-OH) group at either end of the carbon chain is more effective than the primary alcohol of equivalent carbon chain length.

4. The embrittling action of simple ethers is also proportional to carbon chain length, being more effective at the shortest carbon chain

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length. The effectiveness of an (O) group seems not to be much different from a polar (OH) group. The existence of multiple polar (-O-) groups in a complex ether seems to counteract the long carbon chain condition, i.e., these ethers are as effective as short chain simple ethers

5. In the case of alcohols, ethers, and aldehydes extrapolation of embrittlement to zero carbon chain length consistently coincides with the embrittlement potential of water. Water can be regarded as a zero carbon chain length molecule with a polar (-OH) group. This and the aforementioned observations on the lack of influence of ion concentration, are strong evidence that embrittlement by water is not based on stress corrosion electrochemical mechanisms

6. The aldehydes behave as long chain polar molecules in which the (=O) oxygen atom is only somewhat less surface-active than the (-O-) oxygen atom is in ethers.

7. The behavior of alcohols toward aluminum is basically the same as toward steel which would render the potential contribution of hydrogen from the hydrocarbon part of the chain or from the (-OH) group as unlikely, since hydrogen does not embrittle aluminum. Moreover, the extrapolation to zero chain length again coincides with the embrittlement level for water.

V. SOME THOUGHTS ON THE MECHANISM OF EMBRITTLEMENT

A medium disposed at the external surface of a specimen under stress can act as an embrittling agent to the extent that some atoms or molecules in the medium possess a positive interaction capability with the atom of the solid, and to the extent that these atoms or molecules can pursue the crack as it penetrates into the surface of the solid. Thus, there are two qualifying criteria--interaction and mobility.

The nature of the interaction can only be reasonably inferred. Certain foreign atoms are strongly attracted by the surface atoms of the solid. As is the nature of atomic packing, the foreign atom is drawn into the geometrical rest position between the three or four atom surface arrangements of the solid. This must act to increase the interatomic spacing of

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this triplet or quadruplet set by an amount proportional to the force of attraction. This three plus-one or four plus one unit is at a lower state of total free energy, but at the same time the cohesive energy between any two atoms of the solid in this unit is less. Thus, the critical force to separate two atoms of the solid beyond the spacing at which interattraction ceases is reduced. We argue, therefore, that physical adsorption to the real surface of a solid must reduce the cohesive strength at the surface and also the fracture strength. (6,7)

Physical adsorption may not be more than a transition state. The adsorbed atom may migrate into the solid host lattice so that the point of reduced cohesive strength now resides in the interior and possesses no continuity with the source of foreign atoms, i.e., the medium. Alternatively, a change of state may begin at the surface with the growth of a new solid phase with its own crystal lattice. This also acts as a barrier between the solid and the fluid medium to prevent propagation of a ruptured atomic bond. Probably for this reason, liquid metals which have no constitutional propensity for the formation of intermediate phases with the solid will more frequently cause severe embrittlement under stress.

Oxygen must be regarded as strongly interactive with most metals. But normal gaseous oxygen even under special conditions of diatomic dissociation will rapidly form an intervening solid oxide film separating the metal from its environment. However, oxygen in a polar group attached to an organic molecule is in a special state, involving coordinate bonds and two pairs of unshared electrons. While adsorbed to a metal surface, it is jointly bonded both to the host molecule and the metal surface without gain or loss of electrons; i.e., oxidation does not take place. This must prevent any change of state so that in event of atomic separation in the solid surface, the rupture can be followed by the fluid medium with its reservoir of adsorbing species.

It has been recognized for a long time that the real strengths of metals are several orders of magnitude less than their theoretical strengths. The reason for this is, of course, that metals cease to behave purely elastically at quite low stresses and develop a large strain capacity through local plastic shear processes. To the extent that these plastic processes can be

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restrained from initiation, the strength of a metal may approach its theoretical value. The contemporary concepts of the origin of fracture nuclei and crystalline elastic-plastic solid have focused on the unit processes of shear-type plastic strain. These unit plastic processes are doubly heterogeneous in that they are confined to widely separated parallel or conjugate planes and directions and, within each slip plane itself, to an avalanche of separated crystal faults or dislocations moving in the slip direction.

It has been recognized that a line of dislocations contained within a slip plane pushed against a barrier to passage, such as a grain boundary (there are others), by an externally imposed shear stress has many of the elastic stress field characteristics of a sharp crack of equivalent length acted on by transverse stresses. Thus, the tensile stresses directly in front of the head of the pile-up of dislocations are many times greater than the average applied stress. We conceive that a fracture nucleus is formed when these extremely local stress magnifications reach the critical cohesive strength of the solid. When the cohesive strength is highly anisotropic, the fracture assumes a cleavage character.

This part of the discussion served to emphasize that the conditions for fracture nucleation are achieved only at widely separated points. Furthermore, the environment can only influence those critical points at the solid-environment interface. Thus, for efficient embrittlement, the extent to which the surface is tightly packed with polar oxygen groups (or any other surface-active group) is an important factor.

To gain some appreciation of surface packing, it is necessary to give consideration to the shape and character of the whole molecule of which the active group is a part. Water is the simplest case. The (-OH) group is attached only to a hydrogen atom. Here it is important to remember relative atomic sizes. The oxygen atom is so very much larger than the hydrogen atom that the (-OH) group viewed on an atomic scale is hardly more than a slightly distorted oxygen atom. The other appended hydrogen atom is equally insignificant in size. The packing of essentially oxygen atoms (-OH groups) from water onto the surface of a metal is comparatively unobstructed by the size and shape of the molecule.

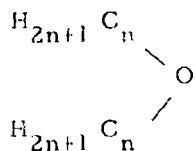
The primary alcohols represent the addition of one finite dimension of shape. These are carbon chains appended to the (-OH) group. Ideally, chain-shaped molecules attached at one end to a planar surface should pack very tightly independent of the length of the chain.

It is doubtful that surface packing is the sole reason for the relationship between chain length and degree of embrittlement. We must consider also the nature of crack propagation. The crack itself is a very narrow planar void. Since the degree of plastic deformation ahead of the advancing crack is small, the separation of fracture surfaces near the crack root may not be more than several atomic distances. Into this constricted channel, the molecules of the organic liquid must penetrate in order to continue propagation of the crack to a length that is self sustaining for the imposed peak stress. It is not difficult to appreciate how the long flexible chain molecules penetrate more slowly than the shorter ones. This penetration factor may, itself, be sufficient to account for the chain length relationship to embrittlement.

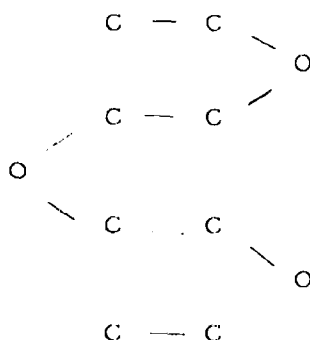
From primary to secondary to tertiary alcohols, there is a progression from one to two to three dimensional characters of the molecular shape. The three-dimensional character of the tertiary alcohols, both from a packing and from a mobility viewpoint, should deter embrittlement and this, in fact, is observed. However, the two-dimensional character of the secondary alcohols is mitigated by the reduction in effective chain length; thus the apparent chain length of secondary propanol is only two, compared to three for n-propyl alcohol. Actually 2-propanol behaves more like n-methyl alcohol, i.e., a reduction of two in chain length. The other secondary alcohols act in similar fashion. There must be another influence of the double carbon atom coordination on the polarizability of the (-OH) group.

This effect of twofold carbon coordination must be an important factor, since the ethers appear to be somewhat more effective embrittling agents than the alcohols. This factor as well as the absence of the screening hydrogen atom (in the -OH group) appears to outweigh the two-dimensional character of the ether molecule. In this regard the notation for an ether of the form $C_nH_{2n+1}OC_nH_{2n+1}$ cannot be indicative of the actual molecular shape. For the oxygen atom to be surface active, the molecular shape must be more of the form

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The substantial embrittling effectiveness of multi-polar ethers such as diethylene glycol diethyl ether suggests that the molecule must assume special shapes to render each of the (O) groups effective and thus to counterbalance the long chain effect. This can be achieved by arrangements as shown:



This chain can be completely flexible, yet present to the surface each of its available (O) groups. In this way strong activity can be developed with decreased volatility.

The importance of the flexible character is seen when a closed ring type structure such as 1,4-dioxane loses ability to produce embrittlement. Structurally, it is virtually impossible for both ethereal oxygen atoms to attach to a single metal surface because of the "staircase" type structure. Both could be adsorbed, however, by two almost touching surfaces as in a crack. Even here, movement of the molecule along either surface would be geometrically prohibited.

This type of work is obviously only at the beginning stage. Some simple generalizations have been revealed, and some rationality can be applied. There is much to be learned about real shape of molecules, their propensities for packing on a planar surface, and their ability to follow an advancing crack. There is also much further exploration of additional polar species capable of engendering embrittlement.

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VI. PERSONNEL AND LOGBOOKS

The work reported herein was performed by Mr. R. Sarocco, Technician, under the supervision of the author. The advice and assistance of Mr. R. Crouse, Senior Chemist, and Mr. J. Garner, Associate Chemist, were vital to the success of the program.

The results reported are contained in ITRI Logbook Nos. C13011, C13536, C13548 and C13549.

Respectfully submitted,

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W. Rostoker

Tech Rev: DJM

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APPENDIX

TEST PROCEDURES

A. Materials

Specimens were cut from 0.080 in. thick commercial sheet. The aluminum 2024 was supplied in the T4 condition. The steel sheet machined to specimen dimensions was heat-treated by austenitizing at 1550°F, cooled in flowing air, and tempered to the required strength. An approximately 0.001 in. root radius was attained in the notches by the use of special files. There was some lack of reproducibility in the steel specimens from heat-treated batch to batch as disclosed by the fatigue limit in water which varied between 450,000 and 700,000 cycles. Only batches giving 550,000 to 650,000 cycles to failure were used.

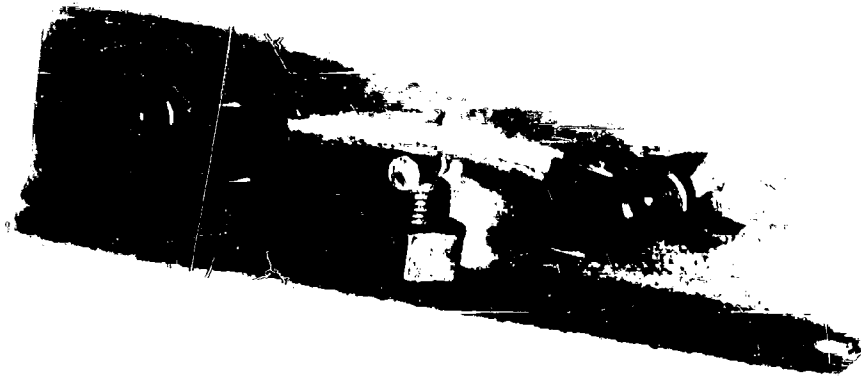
B. Tensile Testing

Flat, sheet type specimens with a 2-in. gage length and pin grips in an Instron machine constituted the simple test procedure. The full stress-strain curve was recorded. The surface of the specimen was polished either chemically (for Al), or by surface grinding (for steel). The candidate liquid was swabbed onto the surface generously before loading.

C. Unnotched Static Loading in Bending

Figure 10 illustrates a bend fixture designed for this research program. The specimen was a strip shaped coupon of dimensions 5 in. long x 0.5 in. wide x 0.080 in. thick. The specimens in the heat-treated condition were ground on the tension surface. Each specimen was loaded to its yield point in the bend fixture by means of an Instron universal testing machine. The load was transferred from the machine to the center pin by means of a threaded nut. The center loading pin transmitted the load to the specimen by a solid glass cylinder, which effectively provided line contact and electrical insulation. Load was transferred from the machine to the loading pin by an intervening steel ball. The steel ball and glass cylinder jointly ensured good axiality of loading. The two outside support pins were covered with insulating tape so that no electrochemical currents could be

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Neg. No. 25005

FIG. 10 - STATIC STRESSING SYSTEM

Stresses at the yield point of the test specimen. Asbestos pad clipped to tension side of the specimen and saturated with candidate embrittling liquid. The whole assembly is placed inside a glass bottle closed with a rubber gasketed steel cap. In the case of saline-base solutions the glass bottle is prerinsed with salt water to minimize evaporation from the pad.

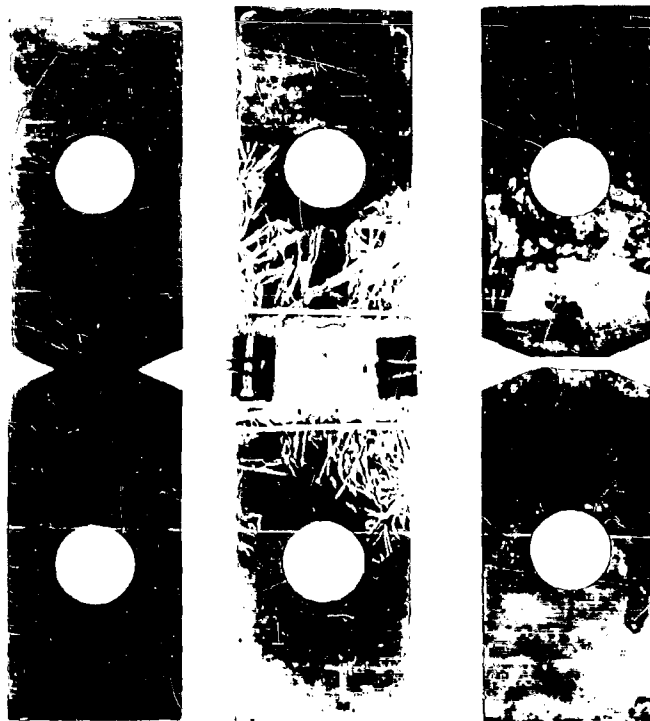
generated between the specimen and the loading fixture

A drop of the candidate fluid was placed on the ground surface of the tension side. With a carbide tool, the ground surface was scraped in a direction transverse to the grinding marks. The tool point is essentially submerged below the candidate fluid to encourage true wetting with the metal. A reservoir of fluid was provided by clamping an asbestos pad, saturated with fluid, to the tension surface on top of the scribe marks. The whole assembly was placed inside a glass bottle and sealed off by means of a rubber gasketed steel cap. This was necessary because of the volatility of some of the fluid candidates. Each test was run for a week, with daily checks for incidence of failure.

D. Cyclic Tension Tension Fatigue Testing

Figure 11 illustrates the type of edge notched specimen used for tension-tension type of fatigue testing and the arrangement of pads, clips, and wrapping by which the candidate organic liquid was brought in contact with the notched region of the specimen. The notch itself was finished to 0.001 in. root radius with special files. Fatigue testing was done in a Baldwin fatigue machine operating at 1800 cpm. According to previous published work, this slow rate of cycling was more conducive to premature cracking in the presence of surfactants.

While the nominal stresses imposed on the edge-notched sheet specimen are not large, the depth of notch and the notch radius (about 0.001 in.) are such as to create very large stress magnifications at the root. If one assumes purely elastic behavior, the stress magnification is probably between 20X and 30X. This means that the stresses at the notch root reach a maximum value of about 400,000 psi.



Neg. No. 25006

FIG. 11 - ILLUSTRATION OF EDGE-NOTCHED SHEET SPECIMEN FOR TENSION-TENSION FATIGUE IN THE PRESENCE OF CANDIDATE ORGANIC EMBRITTLING LIQUIDS. Shows arrangement of liquid-saturated pads clipped to the fracture zone and wrapped to prevent volatilization. Character of fracture also shown.